

## Kinetics of Nucleation of Graphite at different Stages of Solidification for Spheroidal Graphite Iron

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The importance of the nucleation and growth phenomena that control the solidification of castings on the mechanical properties and soundness of cast iron cannot be overemphasized. The graphite nucleation mechanism is directly related to the carbon content of the iron and the inoculation treatment. Over the years, a multitude of theories have been developed with the objective to explain the nucleation process of spheroidal graphite (SG) iron. The most important include the gas bubble theory [1], the graphite or carbon rich cluster theory [2,3], the salt-like carbide theory [4], the silicon carbide theory [5,6], the sulphide/oxide theory [7,8,9,10,11,12], the silicate theory [13,14,15,16].

The heterogeneous nucleation theory is focused on the non-metallic inclusions present in all commercial cast irons. These particles must satisfy some specific conditions to act as possible nucleation sites, including: good crystallographic compatibility, low lattice disregistry or mismatch (no more than 3%), fine dispersion in the melt (1-3  $\mu\text{m}$ ) and high stability at elevated temperatures [14,16].

In this work, interrupted solidification experiments were conducted on spheroidal graphite irons (SG) at three different levels of carbon equivalent, with and without addition of a commercial inoculant. After superheating to 1500°C, the induction-melted iron was treated into the pouring ladle with 1.1 mass % of a FeSiMg alloy (47.2% Si, 6% Mg, 1.15 Ca, 0.24% Al, 0.3% Mn, and 0.88% RE) by the sandwich method. Standard thermal analysis cups were poured. The solidification of the iron in the cup was interrupted by quenching in brine at increasing times (immediately after pouring, after 10 seconds and after 60 seconds). Inoculation was made directly in the cups through the addition of 0.2% of a commercial inoculant (62.6% Si,

0.22% Mg, 1.01% Al, 1.79% Ca, 5.96% Mn, 0.13% Ti, 6.77% Zr, 0.65% Ba and less than 0.07% lanthanides). The chemical analysis of the experimental irons is reported in Table 1. In addition to the elements listed in the table, the alloys contained 0.017% P, 0.04% Cr, 0.01% Mo, 0.07% Cu and less than 0.01% Al and 0.005% Sn.

Table 1. Chemical composition (mass%) of cast irons

heat	CE	C	Si	Mn	Mg	Ti	S
QI	4.38	3.78	1.93	0.22	0.038	0.030	0.009
QII	4.20	3.56	2.03	0.19	0.039	0.021	0.011
QIII	3.93	3.30	2.00	0.19	0.041	0.020	0.010

Scanning electron microscopy (spectrums, mappings, line scan and different detectors) was carried out to analyze and quantify the possible nucleation sites at different solid fractions, as well as the influence of the inoculant in their formation. An example of the use of different detectors to identify nuclei is given in Fig. 1.

Non-metallic inclusions of varying composition have been observed in the matrix and at the centers of graphite nodules of the different irons (Fig. 2). They include silicates, oxides, carbo-nitrides. The complex oxides include Mg, Ce, La (Fig. 2-d). Numerous Ce and lanthanides inclusions were found at the grain boundary without any contact with the graphite.

Over 70% of the inclusions assumed to play a role in graphite nucleation were identified through X-ray composition maps and spectra as (Mg,Ca)S neighboring TiC (Fig. 2-b). This tendency was confirmed in un-inoculated and inoculated irons, independent of iron melt chemistry and of solid fraction. Calcium appears in a great number of sulphides, but less frequent than magnesium. Barium was never found in any nucleation site. A significant number of nuclei included Ti carbo-nitrides that contained Zr in many cases (Fig. 2-c). Most of the time the sulphides appear

to act as nucleation sites for the carbides and at the same time seem to nucleate the graphite.

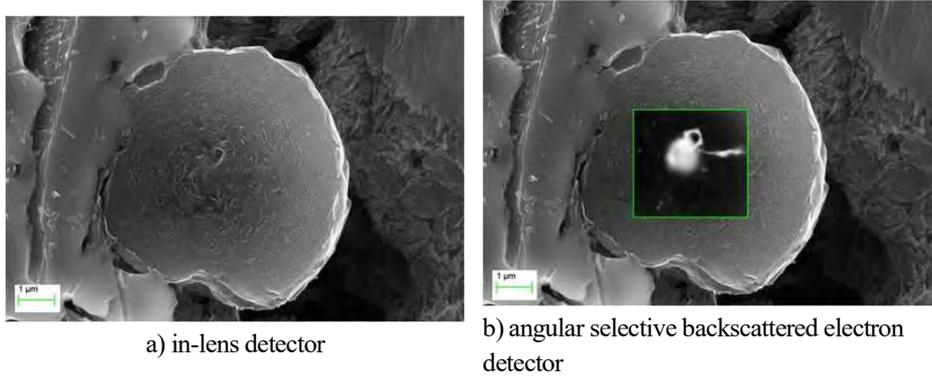


Fig. 1. SEM images of an iron from heat QI under different detectors: sulphide and carbide inclusions were detected

Based on the frequency of occurrence of elements in the 2456 graphite spheroids investigated, and on the thermodynamics free energy of formation calculated with Factsage, it appears that the majority of the nuclei are complex oxy-sulfides of Mg, Ca and sometimes Al (O was found in 76% of the inclusions and S in 17%). While 13.7% inclusions contained MgO, and 11.7% included MgS, 10.3% were Mg oxy-sulfides. A large amount of Ti carbides and carbo-nitrides were also identified (Ti was found in 9.3% of the inclusions). As TiC has a relatively high energy of formation, the Ti compounds are probably more complex carbo-nitrides containing Zr, Al, Si and Mg. Indeed, 6.4% of the inclusions were found to be TiN, out of which 1.8% were (Ti,Zr)N. The number of silicates was very low as only 1% of the inclusions included both Si and O.

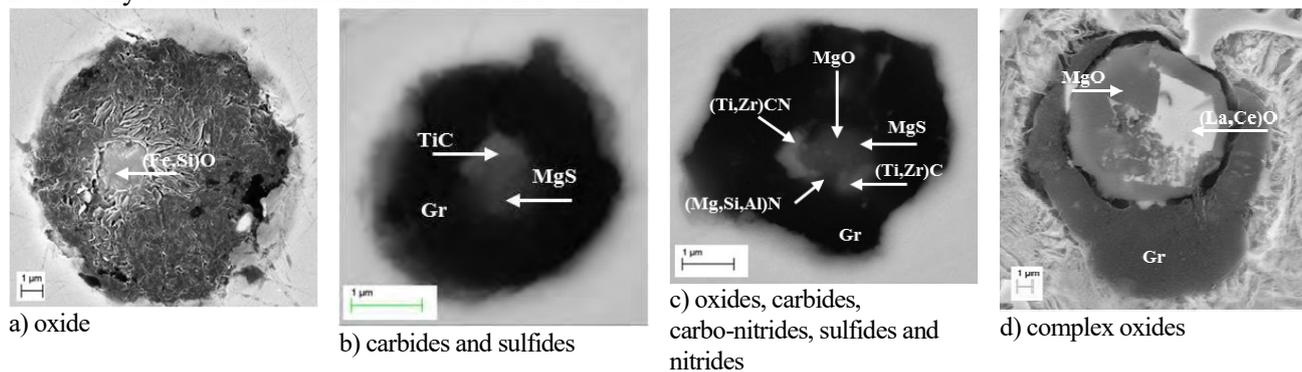


Fig. 2 SEM observations of graphite with different inclusions in the core

Some of the findings in this work are not explained by theories inferring that graphite spheroids nucleate on inclusions that contain an MgS core surrounded by an oxide shell, or with an outer shell of complex Mg silicates, as in many instances the nucleus was made of two or three different compounds, and all of them were in contact with the graphite. MgS and TiC compounds were the major sites for SG nucleation in this work.

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